

Electronic Supplementary Information: Mechanical and physical performance of carbon aerogel reinforced carbon fibre hierarchical composites

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S1 Carbon aerogel synthesis

Carbon aerogel was synthesised as reported previously [1] using commercially-available INDSPEC Chem. Corp. AX-2000 resin, which contains a 73.1 wt. % resorcinol formaldehyde (RF) mixture at a R:F molar ratio of 2:1. Potassium hydroxide (KOH) was used as a catalyst (C). The RF resin composition was kept fixed using an R:C ratio of 50:1 and 40 wt. % RF in the final solution, with the amount of AX-2000 resin, formaldehyde solution, KOH catalyst solution and additional distilled water altered accordingly. Requisite amounts of AX-2000 resin, catalyst and distilled water were mixed and stirred for 15 min and formaldehyde was added drop by drop while stirring to ensure a homogeneous solution. The RF solution was tightly sealed and left

stirring for 3 h at room temperature, during which time gelation had not fully completed. Therefore, the solution could easily infuse into the CF preforms after 3 h.

Either $(0/90)_{5s}$ or $(0/90)_{6s}$ woven CF fabrics were stacked according to the mechanical test to be used (Table S1), with the overall dimensions of the stacked laminate limited by the resin infusion via flexible tooling (RIFT) table and furnace retort (for pyrolysis or thermal desizing). Care was taken to ensure that the all warp and weft tows were aligned, and that the individual plies were not distorted by handling. A vacuum bag was constructed on the RIFT table to accommodate the pre-stacked lamina, initially held in place with bulldog clips, which were then removed, and the bag was then sealed and evacuated. The associated lay-up and inlet/outlet valves are shown in Figures S1 and S2. Details of the materials used for the RIFT process are given in Appendix A.

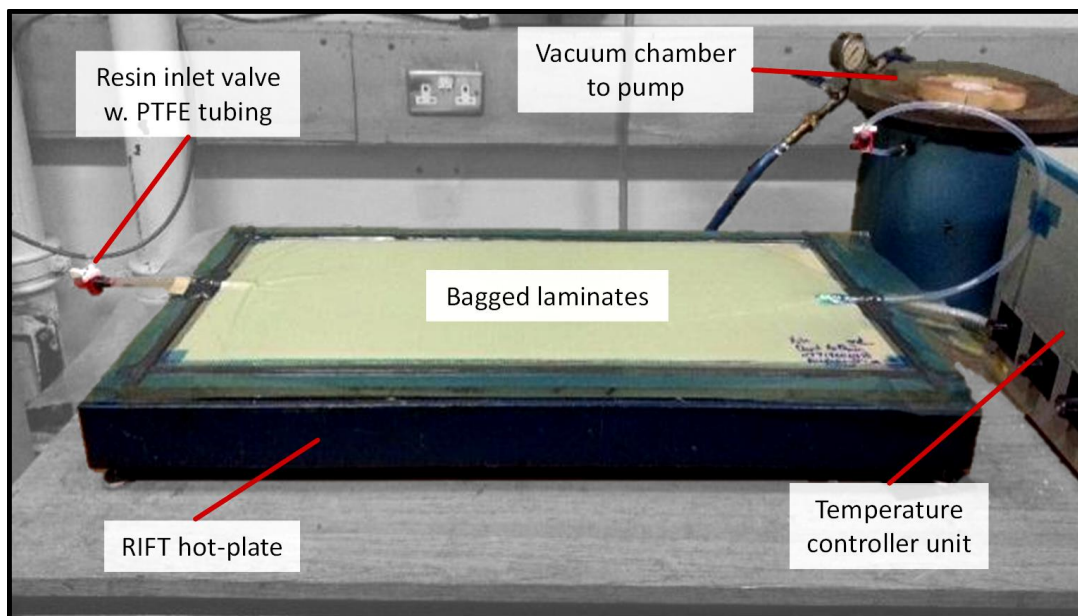


Figure S1 Photograph of RIFT set-up.

Table S1 Nominal laminate dimensions, stacking sequences and tests performed.

Laminate	Contains CAG	Length (mm)	Width (mm)	Thickness (mm)	Lay up	Tests performed
PEGDGE	No	300	200	2.36	(0/90) _{6s}	ILSS
CAG PEGDGE	Yes	300	200	1.88	(0/90) _{5s}	Compression
PRIME	No	300	200	2.33	(0/90) _{6s}	ILSS
CAG PRIME	Yes	300	200	1.77	(0/90) _{5s}	Compression
Baseline	No	345	275	2.52	(0/90) _{6s}	Supplementary Tension
Baseline	No	345	145	2.52	(0/90) _{6s}	Supplementary Compression, ILSS, Density, DMTA, DSC, Thermal diffusivity
Baseline	No	340	140	2.52	(0/90) _{6s}	Density, DMTA, DSC, Thermal diffusivity
Thermally-desized	No	280	240	2.52	(0/90) _{6s}	Supplementary Tension
Thermally-desized	No	310	140	2.52	(0/90) _{6s}	Supplementary Compression
Thermally-desized	No	310	140	2.10	(0/90) _{5s}	Supplementary ILSS, Density, DMTA, DSC, Thermal diffusivity
CAG PRIME	Yes	350	305	2.52	(0/90) _{6s}	Supplementary Tension
CAG PRIME	Yes	350	305	2.52	(0/90) _{6s}	Supplementary Compression, ILSS, Density, DMTA, DSC, Thermal diffusivity
CAG PRIME	Yes	370	325	2.10	(0/90) _{5s}	Density, DMTA, DSC, Thermal diffusivity
CAG PRIME	Yes	370	320	2.10	(0/90) _{5s}	Thermal diffusivity

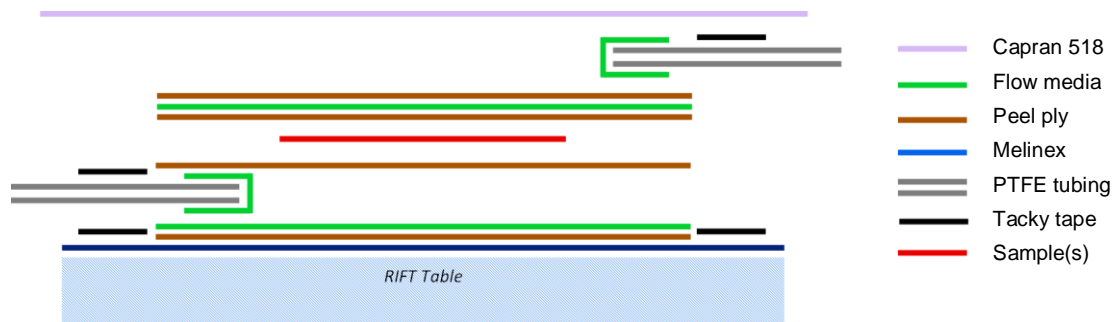


Figure S2 Schematic showing the layers of bagging material and arrangement for RIFT.

For RF RIFT, the outlet valve was closed so that the uptake of resin in the vacuum bag occurred solely via the existing internal vacuum, which was adequate due to the low viscosity of the RF resin. The RF resin was aged at room temperature, 45 °C and then 75 °C for a period of 24 h at each temperature and left to cool for around 4 h to room temperature. After cooling, the vacuum bag containing the laminates was detached from the RIFT table and opened inside a fume hood to vent excess formaldehyde. The laminates were weighed to track the subsequent drying and the opened bag was left overnight inside the fume hood to complete venting. Finally, the laminates were placed for 2-3 days in a vacuum oven at 45 °C.

S2 Pyrolysis of CAG precursor loaded CF fabric, thermal desizing and composite manufacture details

The dried CAG precursor loaded CF laminates were pyrolyzed at 760 °C for 30 min in a Lenton ECF 12/30 furnace under N₂, flowing at 0.5 L/min, to obtain CAG-CF fabrics. Prior to ramping the temperature to 760 °C, the furnace was purged at room temperature under N₂ flowing at 2 l/min for at least 30 min, which was enough to have approximately two complete exchanges prior to the start of heating. The furnace was

heated from room temperature to 760 °C in approximately 3 h, after which the furnace was programmed to switch off after 30 min marking the end of pyrolysis. After pyrolysis, the furnace was left to cool for around 9-10 h under a N₂ flow rate of 0.5 l/min, until approximately 100 °C where the retort door was loosened, and the flow of N₂ stopped. The door was then left ajar to increase the cooling rate and samples were removed when at approximately 50 °C.

After cooling the laminates to room temperature on ceramic plates, the edges of the laminates, which had frayed during the CAG processing, were manually trimmed. The woven CF stack, the monolith CAG-CF preform and the CAG-reinforced CF composite laminates were weighed at each stage of the manufacture to calculate the weight and volume fractions and to determine the CAG loading.

The heat treatment procedure for the ‘thermally-desized’ carbon fibre fabric lamina was the same as that described for the pyrolysis of the CAG precursor loaded laminates.

After degassing the resin in a vacuum oven, the composites were made by infusing the CF fabric, thermally-desized CF fabric and CAG-CF fabrics with resin (Table S2) via RIFT. The processing methodology employed was similar to that described in Section 2 of the main paper, with curing of the PEGDGE at 80 °C for 24 h, and curing of the PRIME resin at ambient for 24 h followed by a 50 °C post cure for 16 h [2]. After infusion, the laminates were weighed to measure the resin uptake, then trimmed.

Table S2 Mechanical properties of PEGDGE [1] and PRIME [2].

Property	Value
PEGDGE tensile modulus	6 MPa
PEGDGE compressive modulus	4 MPa
PEGDGE compressive strength	2 MPa
PRIME tensile modulus	2.98 GPa
PRIME tensile strength	71.2 MPa
PRIME T_g , peak $\tan \delta$, DMA (24 h at RT + 16 h at 50 °C)	88 °C

S3 Mechanical characterisation

The baseline, thermally-desized and CAG composites (Table S1) were tested following ASTM standard test methods for interlaminar shear strength (ILSS) [3] (20 mm length) and longitudinal compression [4] (10 mm gauge length) using an Instron 5969 with a 50 kN load cell in displacement control, at 1 mm/min. The structural composites in the supplementary tests were additionally tested in tension [5], (150 mm gauge length) using an Instron 5985 with a 250 kN load cell in displacement control, at 2 mm/min. The ILSS, compression and tension specimen dimensions were $20 \times 10 \times 2$ or 2.5 mm^3 , $90 \times 10 \times 2$ or 2.5 mm^3 and $250 \times 25 \times 2.5 \text{ mm}^3$, respectively, with the exact thickness depending on the associated laminate, as described in Table S1. Compression and tension specimens had glass fibre composite end tabs bonded to the laminates before cutting into test specimens. For compression, two strain gauges (FLA-2-11, TML, aligned in the loading direction) were adhered using cyanoacrylate glue at the mid-span, to determine whether variations between the front and back strains exceeded the allowed threshold defined in the standard [4] which could have indicated

significant buckling prior to failure. For tensile measurements, one biaxial strain gauge (FCA-10-11, TML) was attached to the centre of one face of the specimen to measure the longitudinal and transverse strains. All tests were conducted at room temperature with at least five valid specimens per material sample to obtain statistically significant results.

The viscoelastic (matrix-dominated) properties were studied using dynamic mechanical thermal analysis (DMTA) (Tritec 2000 DMA, Triton Technology, Laboratory Analytical Instruments) on $30 \times 5 \times 2 \text{ mm}^3$ specimens with a gauge span of 20 mm. A sinusoidal force was applied at 1 Hz and the resulting specimen displacement was measured whilst the temperature was ramped from room temperature to 150 °C at 5 °C/min. The glass transition temperature (T_g) was obtained from the $\tan \delta$ peak, the tangent of the phase angle and the ratio of loss modulus/storage modulus.

S4 Physical characterisation

Fibre volume fractions (v_f) were measured according to ASTM D3171 Method I [6] and composite densities were measured using a Micromeritics AccuPyc 1330 pycnometer with a 10 cm³ nominal cell volume. The specimen width included at least two unit cells of the plain weave CF fabric, in accordance with ASTM standards [7]. Thermal diffusivity was measured by coating test specimens (multilayer (0/90)_{6s}, $8 \times 8 \times 2 \text{ mm}^3$) with graphite spray (Graphit 33, CRC Kontakt Chemie) and using an LFA 447 NanoFlash Light Flash System, according to ASTM E-1461 [8]. The specific heat capacity was obtained by using a differential scanning calorimeter (DSC) (Q2000, Al Tzero pan and hermetic lid, TA Instruments). The thermal conductivity was

calculated as the product of the bulk density, thermal diffusivity and specific heat capacity.

The in-plane and through-thickness electrical conductivities were determined using impedance spectroscopy on square samples cut from the laminates with various sizes, each typically having an area of approximately 1 cm². A Gamry Instruments potentiometer (REF600-23011, Potentiostatic EIS, Gamry Instruments Framework version 6.24 software) was cycled through 10 kHz – 10 Hz, 10 mV rms to measure the conductivities. Resistances were taken within the linear region of the resultant signal (typically at 100 Hz) or by an ohm meter (RS-Components, M210, 611-953, Rhopoint). Silver paint was applied to the connection points to ensure a good electrical contact had been made between the samples and the gold-plated, spring-loaded flat-head probes (RS-Components, 261-5109, 1.3 mm Ø).

The CFs and CAG-CFs were characterised using a high-resolution field emission gun scanning electron microscope (Gemini LEO 1525 FEG-SEM, Carl Zeiss NTS Ltd.) at an acceleration voltage of 5.0 kV. The composite microstructure and fracture surfaces were characterised using a variable pressure scanning electron microscope (Hitachi, S-3400N VP-SEM) at an acceleration voltage of 5.0 kV. The samples were prepared and imaged on Al stubs using silver or carbon tabs from Agar Scientific Ltd. To reduce charging effects, the samples were sputtered with gold at Ar gas pressure 0.1 mbar (20 mA for 45-90 s, 5-10 nm coating) using an Emitech Quorum Technologies K575X Sputter Coater. The specific surface areas (SSA) of the as-received and CAG-CF fabrics were measured using the Brunauer, Emmett and Teller (BET) method with a Micromeritics TriStar 3000 Surface Area and Porosity Analyser after the samples were degassed in N₂ for at least 12 h at 100 °C. Optical microscopy

cross-sections were prepared from ILSS test specimens by mounting the samples in a potting resin and polished to a mirror shine (minimum polishing suspension of 1 μm). It should be noted that the soft nature of the PEGDGE resin meant that these specimens were prone to artifacts introduced by the polishing process.

S5 Densities and compositions of composites for supplementary tests

To investigate the interfacial issues discussed in Section 3, all the composites in the supplementary tests were infused with PRIME epoxy resin. CAG composites were compared to baseline (as-received) CF and control (thermally-desized without CAG) CF composites, as described in Section S2. Unless otherwise stated, all comparisons were made with respect to the baseline (i.e. non-CAG) composite performance.

The densities of the composites, including the weight and volume fractions of their constituents, are presented in Table S3. The CAG composite had a 10 % higher V_f than the baseline, consistent with its slightly higher density. The volume fraction analysis (Table S3) indicated the potential presence of a small fraction of voids (up to 1.5 vol %), possibly associated with tortuous infusion of the resin through the CAG pores. However, the CAG loading on the CAG-CF preform (CAG 8.9 wt % and CF 91.1 wt %) BET SSA ($69.1 \pm 0.6 \text{ m}^2/\text{g}$) and CAG-normalised SSA ($772.8 \pm 15.4 \text{ m}^2/\text{g}$) were similar to that obtained in previous work (CAG 9.5 wt % and CF 90.5 wt %, $80.7 \text{ m}^2/\text{g}$ and $850 \text{ m}^2/\text{g}$, respectively [1]). The high SSA, relative to the as-received carbon fibres ($0.23 \pm 0.004 \text{ m}^2/\text{g}$ [9]), is relevant to applications in structural supercapacitors. The calculation of the effective BET SSA of the CAG in the CAG-CF preforms is presented in Appendix B.

Table S3 Densities and compositions of PRIME matrix composites.

	Density	W _f	W _m	W _a	V _f	V _m	V _a	V _v
	(g/cm ³)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Baseline	1.46	65.6	34.4	0.0	54.4	44.1	0.0	1.5
Thermally-desized	1.47	67.1	32.9	0.0	56.1	42.5	0.0	1.4
CAG	1.51	64.7	28.8	6.5	55.3	38.2	6.1	0.4

W = wt. %, V = vol. %, subscripts: f = fibres, m = matrix, a = aerogel, v = voids

Appendix A Composite manufacturing equipment and materials

- Hotplate, HP 1836, plate size 18" x 36", maximum temperature 260 °C, Wenesco Inc., USA with temperature controller series 9400 with dual display, manufacturers code 940000000, (RS-Components, 312-1863), CAL Controls, GBR and resin flow back vacuum chamber to protect pump, 22 litres, Medina Art Castings Ltd. (Island-Scientific), GBR.
- Capran 518, nylon, thickness 50µm, Cytec Engineered Materials Ltd., GBR.
- Flow media, Knitflow40 (PE) mesh, , Gurit Ltd (SP-High Modulus), GBR.
- Peel-ply, PTFE coated glass fibre FF03PM, 70 g/m², Cytec Engineered Materials Ltd., GBR.
- Melinex 516, polyethylene terephthalate, thickness 50 µm, DuPont, USA.
- PTFE tubing 1025T, (RS-Components, 398-5588), Parker-Legris, FRA.
- SM 5127 Tacky-Tape, silyl-modified adhesive sealant, Schneid-Morehead Inc, USA.
- Flash Tape 1 (FT1), polyester, Cytec Engineered Materials Ltd., GBR.
- Plastic taps (two-way valve), polypropylene/polyethylene, (VWR, 229-7424), Bürkle GmbH, Stuttgart, DEU

Appendix B Calculation of the effective BET SSA contribution of CAG in CAG-CF preforms

The ratio CF : CAG-CF = 1 : 1.098 was determined from the weight differences between the CF before and after CAG infusion and pyrolysis, assuming no loss in the CF during processing.

Total weight of BET sample = 1.0866 g

$$\therefore \text{CF contribution to sample weight} = 1.0866 \text{ g} / 1.098 = 0.98971 \text{ g}$$

$$\therefore \text{CAG contribution to sample weight} = 1.0866 \text{ g} - 0.98971 \text{ g} = 0.09689 \text{ g}$$

$$\text{N.B. CAG wt. \%} = (1.0866 - 0.98971) / 1.0866 = 8.92 \text{ wt. \%}$$

$$\text{BET SSA of CF} = 0.227 \text{ m}^2/\text{g} \pm 0.004 \text{ m}^2/\text{g}$$

$$\text{Total BET SSA of CAG-CF sample} = 69.139 \text{ m}^2/\text{g} \pm 0.6443 \text{ m}^2/\text{g}$$

$$\therefore \text{CAG BET SSA contribution as wt. \%}$$

$$= ((69.139 \text{ m}^2/\text{g} [\text{CAG-CF}] - 0.227 \text{ m}^2/\text{g} [\text{CF}]) / 8.92 \text{ wt. \%}) \times 100 = 772.8 \text{ m}^2/\text{g}$$

$$\therefore \text{CAG contribution error}$$

$$= 772.8 \text{ m}^2/\text{g} \times \sqrt{((0.643 \text{ m}^2/\text{g} / 69.139 \text{ m}^2/\text{g})^2 + (0.004 \text{ m}^2/\text{g} / 0.227 \text{ m}^2/\text{g})^2)} = 15.4 \text{ m}^2/\text{g}$$

Densities of constituents

$$\text{CF} \quad 1.76 \text{ g/cm}^3$$

$$\text{CAG} \quad 1.58 \text{ g/cm}^3$$

$$\text{CF + CAG} \quad 1.71 \text{ g/cm}^3$$

$$\text{Epoxy resin (cured)} \quad 1.14 \text{ g/cm}^3$$

Appendix C DMTA profiles

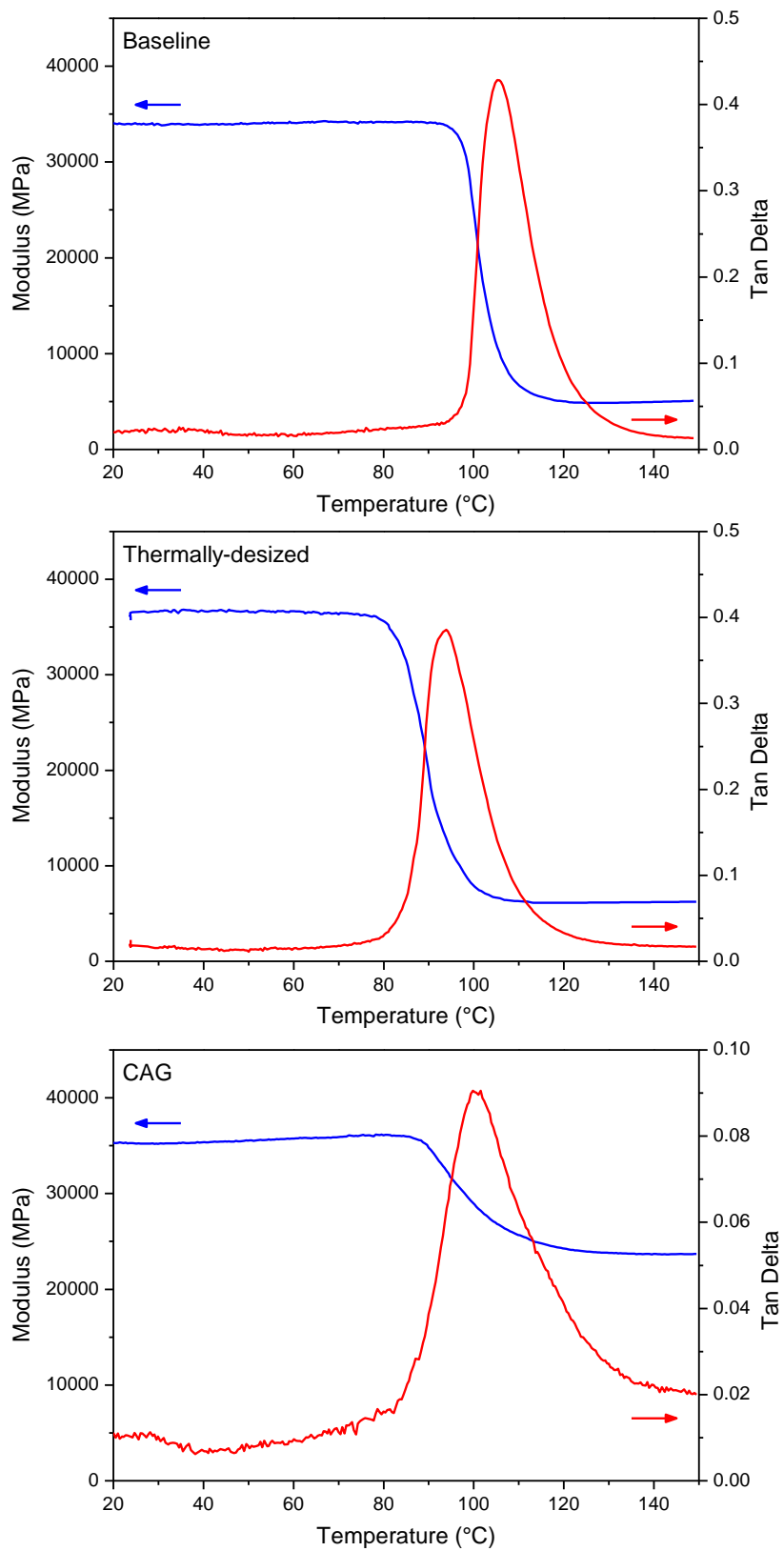


Figure S3 Typical dynamic mechanical thermal analysis profiles.

Appendix D BET SSA isotherms

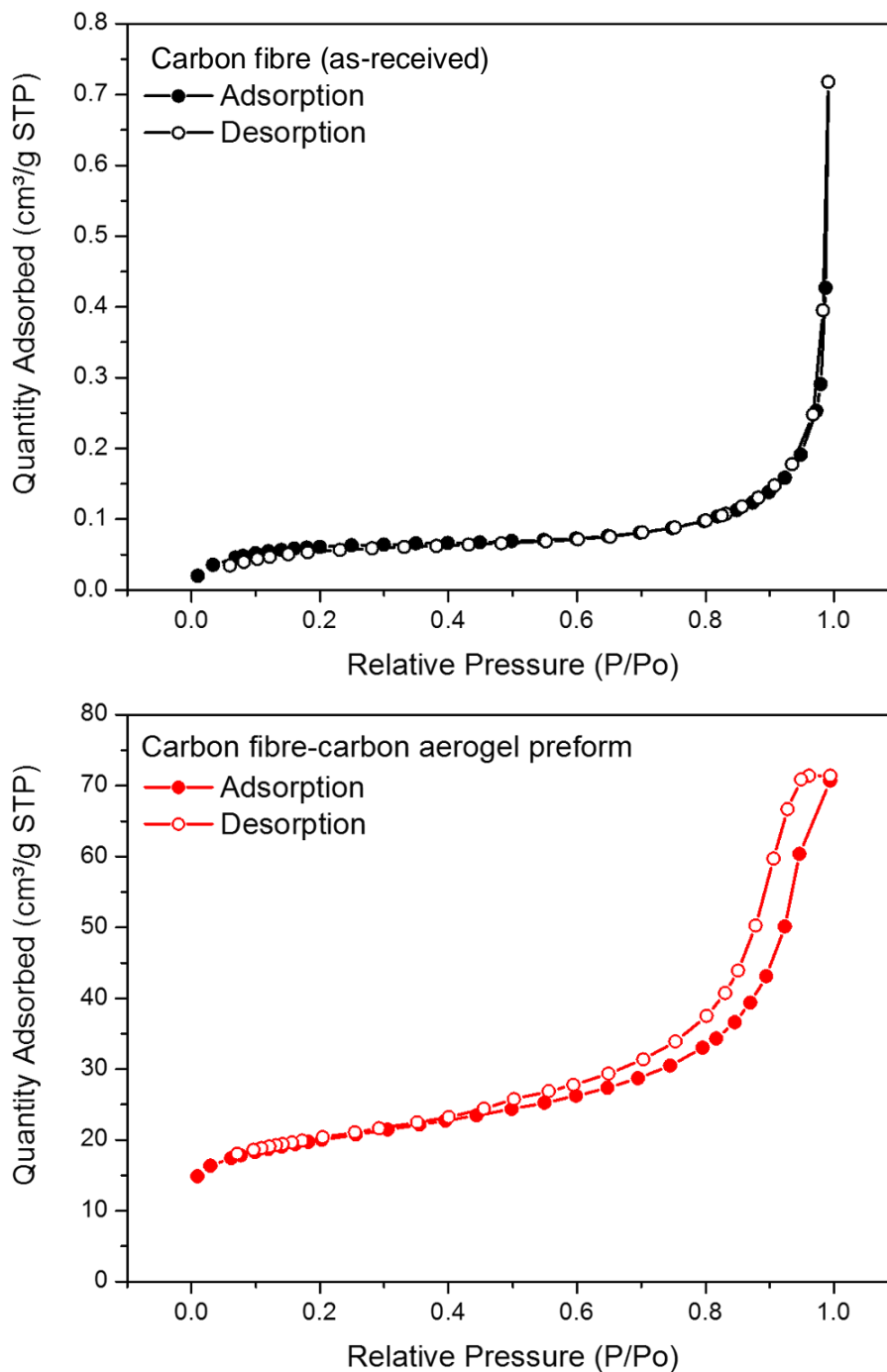


Figure S4 Brunauer, Emmett and Teller (BET) Specific surface area isotherms of as-received carbon fibre weave and carbon fibre-carbon aerogel preform displaying a Type II isotherm, and a Type IV isotherm, respectively, in accordance with the IUPAC classification.

References

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Supplementary figure and table captions

Figure S1 Photograph of RIFT set-up.

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Table S1 Nominal laminate dimensions, stacking sequences and tests performed.

Table S2 Mechanical properties of PEGDGE (26) and PRIME (28).

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